

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
4 April 2002 (04.04.2002)

PCT

(10) International Publication Number  
**WO 02/26378 A1**

(51) International Patent Classification<sup>7</sup>: **B01J 19/08**

(74) Agent: **TRACY, Emery, L.**; P.O. Box 1518, Boulder, CO 80306 (US).

(21) International Application Number: **PCT/US01/30110**

(22) International Filing Date:  
26 September 2001 (26.09.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/235,998 27 September 2000 (27.09.2000) US

(71) Applicant (for all designated States except US): **UNIVERSITY OF WYOMING** [US/US]; 16th and Gibbon, Laramie, WY 82071 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **AGARWAL, Pradeep, K.** [US/US]; 2121 East Curtis Street, Laramie, WY 82072 (US). **LINJEWILE, Temi, M.** [TZ/US]; 570 West Murray Boulevard #3S, Murray, UT 84123 (US).

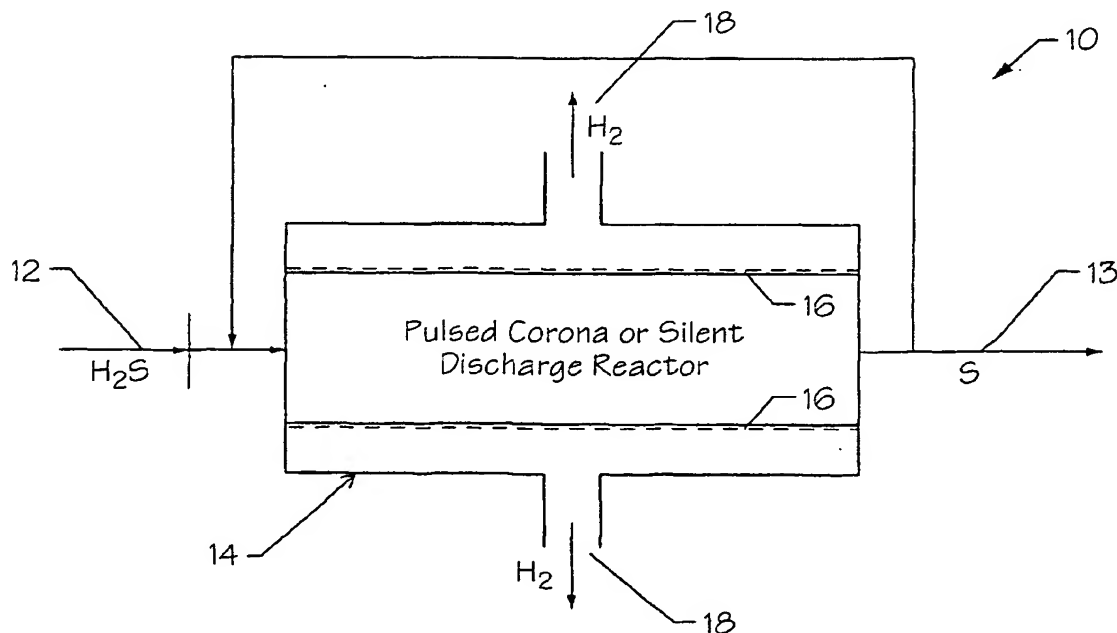
(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:  
— with international search report

[Continued on next page]

(54) Title: **CONVERSION OF METHANE AND HYDROGEN SULFIDE IN NON-THERMAL SILENT AND PULSED CORONA DISCHARGE REACTORS**



(57) Abstract: A method for producing hydrogen (18) from raw feed gases (12). The method comprises providing a reactor (14), positioning reactor walls (16) within the reactor (14), introducing the raw feed gases (12) into the reactor (14), and reacting the raw feed gases (12) within the reactor (14) to produce hydrogen (18). An apparatus (10) for the production of hydrogen (18) using a reactor (14) is also provided.

AL



— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

CONVERSION OF METHANE AND HYDROGEN SULFIDE IN NON-THERMAL SILENT  
AND PULSED CORONA DISCHARGE REACTORS1 BACKGROUND OF THE INVENTION2 1. Field of the Invention

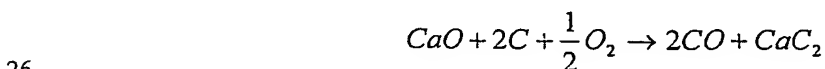
3 This invention relates generally to the production of higher C<sub>2</sub> and C<sub>3</sub>  
4 hydrocarbons and to the production of elemental sulfur, accompanied by the  
5 simultaneous recovery of hydrogen, from feedstreams containing methane and  
6 hydrogen sulfide and, more particularly, it describes a new process for the production  
7 of acetylene from methane and the production of hydrogen and elemental sulfur from  
8 hydrogen sulfide in silent and pulsed corona discharge reactors by continuously  
9 recovering hydrogen from the gaseous mixture of products and reactants through a  
10 membrane wall.  
11

12 2. Description of the Prior Art

13 The principal impetus behind the synthesis of acetylene arises from its value as  
14 a chemical intermediate. In the early 1900's, acetylene was used as a raw material in  
15 the production of chlorinated solvents, acetic anhydride, and acid, as well as acetone.  
16 Starting in 1930's, acetylene was also used as the starting material for a variety of  
17 polymers such as synthetic rubbers, vinyl acetate and vinyl chloride monomers  
18 required for PVA and PVC, water-base paints, dry-cleaning solvents, and aerosol  
19 insecticides.  
20 Two principal routes have been described in the literature for the commercial  
21 production of acetylene:

- 22 • **Hydrolysis of calcium carbide formed from the reduction of lime**  
23 **with carbon**

24 Calcium oxide is one of the most stable metal oxides. Production of calcium  
25 carbide using the following reaction, then, requires significant expenditure of energy.



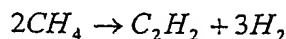
27 Not surprisingly, the majority of earlier technological improvements related to the  
28 development of the reduction furnace. The hydrolysis reaction:



30 is highly exothermic. Temperature control is vital to prevent decomposition of  
31 acetylene.

1           •       **Cracking of hydrocarbons, in particular methane, at high**  
2                   **temperatures**

3           More recently, cracking processes for producing acetylene have received  
4   significant attention. Methane is used, most often, as the feedstock; other  
5   hydrocarbon sources are not available as readily. Several techniques have been  
6   described in the literature; however, two key limitations appear to be common to most  
7   of these methods. First, acetylene is diluted considerably by reaction products. For  
8   example, consider the reaction:



10   The maximum possible concentration of acetylene, at 100% conversion of methane, is  
11   twenty-five (25 vol.%) volume percent. Second, for acetylene production to be  
12   favored thermodynamically, the reaction temperature should be greater than about two  
13   thousand (2000 °K) degrees Kelvin. At this temperature, conversion to acetylene is  
14   rapid; however, sequential decomposition of acetylene to carbon and hydrogen is  
15   rapid as well. Clearly, recovery of the acetylene intermediate requires rapid  
16   quenching of the product gases. This is difficult in practice since the thermal capacity  
17   of gases is low.

18           The several thermal methods described in the literature for cracking of  
19   hydrocarbons to produce acetylene include the following:

- 20
- 21           •       *Electric arc:* This method provides comparatively easy heating of  
22                   gases to the appropriate reaction temperature. The hot zone, however,  
23                   can be spatially irregular leading to excessive product decomposition.  
24
- 25           •       *Partial oxidation:* The raw material is combined with just  
26                   sufficient oxidizing gas to release the thermal energy required for  
27                   achieving and maintaining the desired reaction temperature.  
28                   Quenching of gases remains difficult though product dilution can be  
29                   minimized by use of oxygen.  
30
- 31           •       *Regenerative pyrolysis:* In this method, a structure of refractory  
32                   shapes is heated through intermittent flow of oxidizing gas. In between

the periods corresponding to oxidizing gas flow, hydrocarbons contact the heated surfaces and undergo endothermic pyrolytic cracking.

- *Submerged flame:* A flame is propagated in within the bulk of a liquid hydrocarbon. The high temperature required for reaction is achieved in the flame region. Quenching is rapid.

Other thermal methods – for example, triboelectric discharge and laser irradiation – have also been described more recently in the patent literature. Expensive and potentially corrosive reaction chamber is necessary for laser irradiation; and triboelectric discharge involves potentially dangerous pressure changes.

Non-thermal discharges have attempted to overcome the shortcomings of thermal methods. Such non-equilibrium plasmas have been divided into five distinctive groups depending on the mechanism used for their generation, applicable pressure range, and electrode geometry. These are as follows:

- *Glow discharge:* This is an essentially low-pressure phenomenon usually between flat electrodes. The low pressure and mass flow severely restrict chemical industrial application.
- *Corona Discharge:* Use of inhomogeneous electrode geometries permits stabilization of discharges at high pressure. Several specific regions of operation – for example, ac or dc, and pulsed – have been described in the literature for applications involving, most often, cleanup of flue gas and atmospheric pollutants. The use of dc corona discharges for the production of acetylene from methane has been described. The AC/DC corona discharges, however, are inefficient in their higher energy consumption. The use of pulsed corona discharges for the production of acetylene from methane is one of the embodiments of the present patent application.

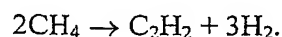
- 1           •     *Silent Discharge:*     In this operational regime, one or both of the  
2                     electrodes are covered with a dielectric layer. Application of a  
3                     sinusoidal (or other time-varying) voltage, then, leads to pulsing  
4                     electric fields and microdischarges similar to those observed in pulsed  
5                     corona discharge systems.  
6
- 7           •     *RF Discharge:*         In such systems, the electrodes are not an  
8                     integral part of the discharge volume. Non-thermal (or non-  
9                     equilibrium) conditions are expected only at low pressures whereas  
10                    thermal plasmas, with the limitations discussed earlier, can be expected  
11                    at high pressures – and larger production rates – of interest in the  
12                    chemical process industry.  
13
- 14          •     *Microwave Discharge:*     Here, similar to RF discharge systems,  
15                    the electrodes are not an integral part of the discharge volume. The  
16                    wavelength of the applied electromagnetic field becomes comparable  
17                    to the dimensions of the discharge volume and necessitates other  
18                    coupling mechanisms. Several patents have been issued on the use of  
19                    microwave energy for the production of acetylene from methane. Used  
20                    metal/non-metal composites (elongated structural construction) within  
21                    the discharge volume and a pulsating microwave energy source have  
22                    been described. Using similar internals in the discharge volume but  
23                    with a continuous microwave energy source has also been described.  
24                    Other catalytic materials have also been used within the discharge  
25                    volume. The use of activated charcoal as catalyst/reactant within the  
26                    discharge volume has been described. The use of catalytic pellets  
27                    within the discharge volume can lead to deposition of carbon on the  
28                    internal surfaces and, therefore, intermittent operation. Others have,  
29                    consequently, generated plasma using microwave energy; this plasma  
30                    was introduced into a reactor loaded with catalyst.  
31

32           In comparing these non-thermal plasmas, it must be noted that in a glow  
33     discharge, the electrons gain energy from the applied field. Due to low pressures,

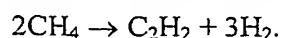
collision with neutral species is infrequent. Propensity for the creation of reactive ions and chemical species is limited. Steady state operation is governed, primarily, by loss of energy incurred by the electrons on enclosure walls and other surfaces within the reactor. The situation is similar in RF and microwave discharges. In corona and silent discharges, the situation is entirely different; these are the operating regimes that are embodied in the present patent application. The fast electrons do indeed transfer energy to other molecules in the system. Electrode geometry and construction prevent sparking or arcing. Propensity for the creation of reactive ions and chemical species is very high.

#### SUMMARY

The present invention is a method for the production of acetylene. The method comprises providing raw feed gases consisting of methane, introducing the raw feed gases into a reactor, positioning reactor walls within the reactor, and reacting the raw feed gases within the reactor with the following reaction:

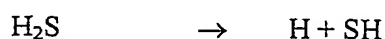


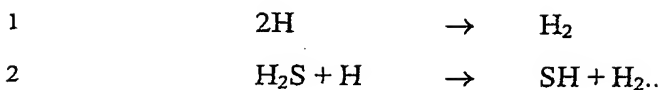
The present invention additionally including an apparatus for the production of acetylene. The apparatus comprises raw feed gases consisting of methane, a reactor for reacting the raw feed gases within the reactor, and reactor walls positioned within the reactor wherein the following reaction occurs:



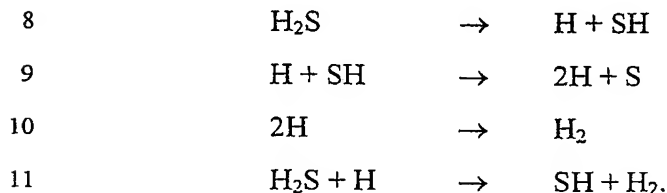
The present invention further includes a method for producing hydrogen from raw feed gases. The method comprises providing a reactor, positioning reactor walls within the reactor, introducing the raw feed gases into the reactor, and reacting the raw feed gases within the reactor to produce hydrogen.

The present invention further still includes a method for the production of hydrogen and elemental sulfur. The method comprises providing raw feed gases consisting of hydrogen sulfide ( $\text{H}_2\text{S}$ ), introducing the raw feed gases into a reactor, positioning reactor walls within the reactor, and reacting the raw feed gases within the reactor with at least one of the following reactions:





3 The present invention further yet includes an apparatus for the production of  
4 hydrogen and elemental sulfur. The apparatus comprises raw feed gases consisting of  
5 hydrogen sulfide ( $\text{H}_2\text{S}$ ), a reactor for reacting the raw feed gases within the reactor,  
6 and reactor walls positioned within the reactor wherein at least one of the following  
7 reactions occur:



### 13 BRIEF DESCRIPTION OF THE DRAWINGS

14 FIG. 1 is a schematic view of the apparatus and method for the conversion of  
15 methane in non-thermal silent and pulsed corona discharge reactors, constructed in  
16 accordance with the present invention; and

17 FIG. 2 is a schematic view of the apparatus and method for the conversion of  
18 hydrogen sulfide in non-thermal silent and pulsed corona discharge reactors,  
19 constructed in accordance with the present invention.

### 21 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

22 The present invention concerns utilizing either a non-thermal pulsed plasma  
23 corona reactor or a silent barrier reactor having membranes positioned therein and  
24 receiving co-axial or other gas flow patterns. The present invention permits collection  
25 of purified hydrogen and provides significant energy and conversion advantages.

26 As illustrated in FIG. 1, the present invention is an apparatus and method,  
27 indicated generally at 10, for the production of acetylene 11 (and other  $\text{C}_2$  and  $\text{C}_3$   
28 hydrocarbons), using methane as a raw feed gas 12, and for the production of  
29 elemental sulfur and hydrogen using hydrogen sulfide ( $\text{H}_2\text{S}$ ) as a raw feed gas 12,  
30 both in a silent discharge and non-thermal pulsed plasma corona reactor 14. It should  
31 be noted that the present invention can utilize either a silent discharge reactor or a  
32 non-thermal pulsed corona reactor.



The raw feed gas 12 is available in sour natural gas streams and the production facility for producing the acetylene 11 and the hydrogen and elemental sulfur can be sited, to advantage, near such gas fields. The principal overall reaction for production of the acetylene 11 within the non-thermal pulsed plasma corona reactor 14 is as follows:



Within the non-thermal pulsed plasma corona reactor 14, conversion is expected to proceed through the dissociation of methane and hydrogen sulfide by energetic electrons according to the following:



The recombination of the radical species leads to the following:



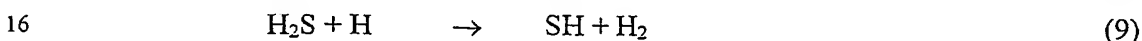
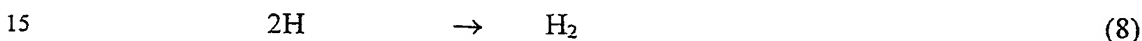
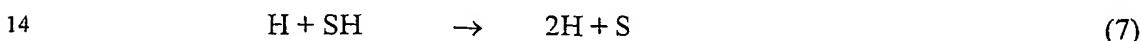
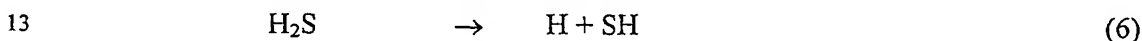
High voltage pulses in the non-thermal pulsed plasma corona reactor 14 produce short-lived microdischarges that preferentially accelerate the electrons without imparting significant energy to the ions. The high voltage pulses within the non-thermal pulsed plasma corona reactor 14 lowers power consumption. In addition, most of the energy applied goes to accelerating the electrons rather than the comparatively massive ions. Larger reactor volumes are consequently possible.

The non-thermal pulsed plasma corona reactor 14 has reactor walls 16 constructed from membrane materials – for example, palladium coated substrates, carbon among others – which permit selective permeation of hydrogen 18. Continuous removal of hydrogen 18 through the reactor walls 16 pushes *reaction A*

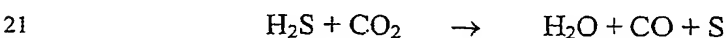
1 towards completion. The membrane materials can be coated with a corrosive resistant  
2 material such as platinum or the like.

3 A schematic diagram illustrating the apparatus and method of the present  
4 invention is illustrated in FIG. 1. It should be noted, however, that alternative  
5 arrangements devised to exploit the process concept more advantageously are within  
6 the scope of this invention.

7 As illustrated in FIG. 2, and as described above, the present invention further  
8 includes the conversion of hydrogen sulfide 13 to elemental sulfur 13 and hydrogen 18  
9 in a non-thermal pulsed corona reactor 14. The H<sub>2</sub>S, CO<sub>2</sub>, and CH<sub>4</sub> from a  
10 regenerator (not shown) will form the primary feed to the non-thermal pulsed corona  
11 reactor 14. Recovery of elemental sulfur 22 and hydrogen 18 from H<sub>2</sub>S in the non-  
12 thermal pulsed corona reactor 14 is based, primarily, on the following reactions:



17 The emphasis is on the dissociation of H<sub>2</sub>S according to Reaction (6).  
18 Formation of sulfur occurs by Reaction (7). Reactions (8) and (9) are responsible for  
19 the formation of hydrogen. Since the feed gas stream to the non-thermal pulsed  
20 corona reactor 14 consists of H<sub>2</sub>S and CO<sub>2</sub>, the following reaction can also take place:



22 (10).

23 The approach herein has a distinct advantage in that the fuel value of H<sub>2</sub>S is  
24 transformed to CO and H<sub>2</sub>; this synthesis gas can actually be burnt to meet the energy  
25 requirements of the process. While CO<sub>2</sub> also leads to the formation of COS, its  
26 production can be minimized by choice of proper operating conditions.

27 The reactions and processes described herein can also be viewed as a  
28 substitute for the Claus chemistry and operations used widely for sulfur recovery from  
29 streams containing hydrogen sulfide.

30 The advantages of the apparatus and process 10 of the present invention are  
31 clear:

- 1     • The present invention permits the production of acetylene (and other C<sub>2</sub> and C<sub>3</sub>  
2 hydrocarbons) 11 and elemental sulfur 22 and hydrogen 18 from relatively  
3 inexpensive feedstock. Expensive preheating and pressurization of the feed gases 12  
4 is also not required. The hydrogen 18 separation is relatively simple.
- 5     • The present invention permits simultaneous production of hydrogen 18. The fuel  
6 value of methane is recovered in the form of cleaner-burning hydrogen. The hydrogen  
7 14 can find use within the petroleum refinery if the process is used in conjunction with  
8 a desulfurization unit. Alternatively, hydrogen 14 can be used to generate clean  
9 electricity using fuel-cell technology.

10           The present invention can be utilized for methane, hydrogen sulfide, or  
11 mixtures thereof, along with other gases. The products, besides the hydrogen, will  
12 vary with operating conditions and feed mixture composition. Also, the present  
13 invention can be integrated readily into fuel cell applications.

14           The foregoing exemplary descriptions and the illustrative preferred  
15 embodiments of the present invention have been explained in the drawings and  
16 described in detail, with varying modifications and alternative embodiments being  
17 taught. While the invention has been so shown, described and illustrated, it should be  
18 understood by those skilled in the art that equivalent changes in form and detail may  
19 be made therein without departing from the true spirit and scope of the invention, and  
20 that the scope of the present invention is to be limited only to the claims except as  
21 precluded by the prior art. Moreover, the invention as disclosed herein, may be  
22 suitably practiced in the absence of the specific elements which are disclosed herein.

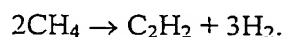
23

1

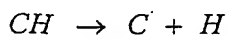
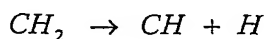
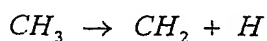
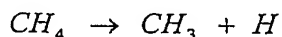
CLAIMS

What is claimed is:

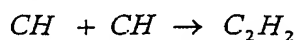
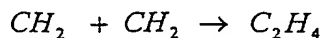
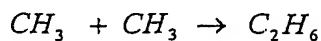
1. A method for the production of acetylene, the method comprising:  
 providing raw feed gases consisting of methane;  
 introducing the raw feed gases into a reactor;  
 positioning reactor walls within the reactor; and  
 reacting the raw feed gases within the reactor with the following reaction:

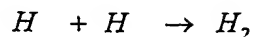


2. The method of claim 1 wherein the reactor is selected from the group consisting of a non-thermal pulsed plasma corona and a silent discharge reactor.
3. The method of claim 1 wherein the raw feed gases are collected from sour natural gas streams.
4. The method of claim 1 wherein the reaction within the reactor proceeds through the dissociation of methane by energetic electrons according to the following reactions:



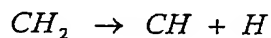
5. The method of claim 4 wherein the recombination of the radical species proceeds according to the following reactions:



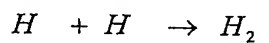
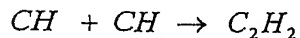
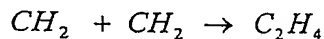
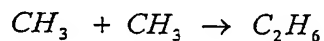


6. The method of claim 1 and further comprising:  
high voltage pulses in the reactor, the high voltage pulses producing short-lived microdischarges that accelerate the electrons without imparting significant energy to the ions.
7. The method of claim 1 wherein the reactor walls are constructed from membrane materials, the membrane materials allowing selective permeation of hydrogen for continuous removal of hydrogen through the membrane materials.
8. The method of claim 7 wherein the membrane materials are selected from the group consisting of palladium coated substrates and carbon.
9. The method of claim 8 and further comprising:  
coating the membrane materials with a corrosive resistant material.
10. The method of claim 8 wherein the corrosive resistant material is constructed from a platinum material.
11. An apparatus for the production of acetylene, the apparatus comprising:  
raw feed gases consisting of methane;  
a reactor for reacting the raw feed gases within the reactor; and  
reactor walls positioned within the reactor;  
wherein the following reaction occurs:  
$$2CH_4 \rightarrow C_2H_2 + 3H_2$$
12. The apparatus of claim 11 wherein the reactor is selected from the group consisting of a non-thermal pulsed plasma corona and a silent discharge reactor.
13. The apparatus of claim 11 wherein the raw feed gases are collected from sour natural gas streams.

14. The apparatus of claim 11 wherein the reaction within the reactor proceeds through the dissociation of methane by energetic electrons according to the following reactions:



15. The apparatus of claim 14 wherein the recombination of the radical species proceeds according to the following reactions:



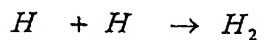
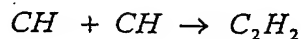
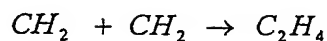
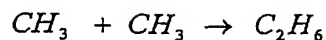
16. The apparatus of claim 11 wherein the reactor includes high voltage pulses, the high voltage pulses producing short-lived microdischarges that accelerate the electrons without imparting significant energy to the ions.

17. The apparatus of claim 11 wherein the reactor walls are constructed from membrane materials, the membrane materials allowing selective permeation of hydrogen for continuous removal of hydrogen through the membrane materials.

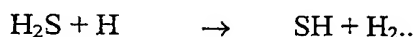
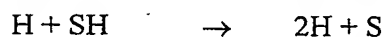
18. The apparatus of claim 17 wherein the membrane materials are selected from the group consisting of palladium coated substrates and carbon among others.

19. The apparatus of claim 18 and further comprising:  
coating the membrane materials with a corrosive resistant material.

20. The apparatus of claim 19 wherein the corrosive resistant material is constructed from a platinum material.
21. A method for producing hydrogen from raw feed gases, the method comprising:
- providing a reactor;
  - positioning reactor walls within the reactor;
  - introducing the raw feed gases into the reactor; and
  - reacting the raw feed gases within the reactor to produce hydrogen.
22. The method of claim 21 wherein the reactor is selected from the group consisting of a non-thermal pulsed plasma corona and a silent discharge reactor.
23. The method of claim 21 wherein the raw feed gases are collected from sour natural gas streams.
24. The method of claim 21 wherein the raw feed gases consist of methane and hydrogen sulfide are reacted within the non-thermal pulsed plasma corona reactor with the following reaction:
- $$\text{CH}_4 + \text{H}_2\text{S} \rightarrow \text{CH}_3\text{SH} + \text{H}_2$$
- to produce hydrogen.
25. The method of claim 24 wherein the reaction within the non-thermal pulsed plasma corona reactor proceeds through the dissociation of methane by energetic electrons according to the following reactions:
- $$\begin{aligned}\text{CH}_4 &\rightarrow \text{CH}_3 + \text{H} \\ \text{CH}_3 &\rightarrow \text{CH}_2 + \text{H} \\ \text{CH}_2 &\rightarrow \text{CH} + \text{H} \\ \text{CH} &\rightarrow \text{C} + \text{H}\end{aligned}$$
26. The method of claim 25 wherein the recombination of the radical species proceeds according to the following reactions:

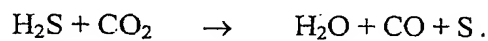


27. The method of claim 21 wherein the raw feed gases consist of hydrogen sulfide ( $H_2S$ ) are reacted within the reactor with one of the following reactions:



to produce hydrogen.

28. The method of claim 27 wherein the reaction within the reactor proceeds through the dissociation of hydrogen sulfide by energetic electrons according to the following reaction:



29. The method of claim 21 and further comprising:  
high voltage pulses in the reactor, the high voltage pulses producing short-lived microdischarges that accelerate the electrons without imparting significant energy to the ions.

30. The method of claim 21 wherein the reactor walls are constructed from membrane materials, the membrane materials allowing selective permeation of hydrogen for continuous removal of hydrogen through the membrane materials.

31. The method of claim 27 wherein the membrane materials are selected from the group consisting of palladium coated substrates and carbon among others.

32. The method of claim 31 and further comprising:  
coating the membrane materials with a corrosive resistant material.



33. The method of claim 32 wherein the corrosive resistant material is constructed from a platinum material.

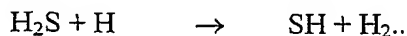
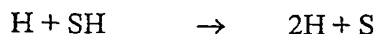
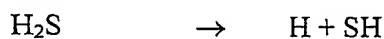
34. A method for the production of hydrogen and elemental sulfur, the method comprising:

providing raw feed gases consisting of hydrogen sulfide ( $\text{H}_2\text{S}$ );

introducing the raw feed gases into a reactor;

positioning reactor walls within the corona reactor; and

reacting the raw feed gases within the reactor with at least one of the following reactions:



35. The method of claim 34 wherein the reactor is selected from the group consisting of a non-thermal pulsed plasma corona and a silent discharge reactor.

36. The method of claim 34 wherein the raw feed gases are collected from sour natural gas streams.

37. The method of claim 34 wherein the reaction within the reactor proceeds through the dissociation of hydrogen sulfide by energetic electrons according to the following reaction:



38. The method of claim 34 and further comprising:

high voltage pulses in the reactor, the high voltage pulses producing short-lived microdischarges that accelerate the electrons without imparting significant energy to the ions.

39. The method of claim 34 wherein the reactor walls are constructed from membrane materials, the membrane materials allowing selective permeation of hydrogen for continuous removal of hydrogen through the membrane materials.
40. The method of claim 39 wherein the membrane materials are selected from the group consisting of palladium coated substrates and carbon.
41. The method of claim 40 and further comprising:  
coating the membrane materials with a corrosive resistant material.
42. The method of claim 41 wherein the corrosive resistant material is constructed from a platinum material.
43. An apparatus for the production of hydrogen and elemental sulfur, the apparatus comprising:  
raw feed gases consisting of hydrogen sulfide ( $\text{H}_2\text{S}$ );  
a reactor for reacting the raw feed gases within the reactor; and  
reactor walls positioned within the reactor;  
wherein at least one of the following reactions occur:
- $$\begin{array}{lll} \text{H}_2\text{S} & \rightarrow & \text{H} + \text{SH} \\ \text{H} + \text{SH} & \rightarrow & 2\text{H} + \text{S} \\ 2\text{H} & \rightarrow & \text{H}_2 \\ \text{H}_2\text{S} + \text{H} & \rightarrow & \text{SH} + \text{H}_2. \end{array}$$
44. The apparatus of claim 43 wherein the reactor is selected from the group consisting of a non-thermal pulsed plasma corona and a silent discharge reactor.
45. The apparatus of claim 43 wherein the raw feed gases are collected from sour natural gas streams.
46. The apparatus of claim 43 wherein the reaction within the reactor proceeds through the dissociation of hydrogen sulfide by energetic electrons according to the following reactions:



47. The apparatus of claim 43 wherein the reactor includes high voltage pulses, the high voltage pulses producing short-lived microdischarges that accelerate the electrons without imparting significant energy to the ions.
48. The apparatus of claim 43 wherein the reactor walls are constructed from membrane materials, the membrane materials allowing selective permeation of hydrogen for continuous removal of hydrogen through the membrane materials.
49. The apparatus of claim 48 wherein the membrane materials are selected from the group consisting of palladium coated substrates and carbon among others.
50. The apparatus of claim 49 and further comprising:  
coating the membrane materials with a corrosive resistant material.
51. The apparatus of claim 50 wherein the corrosive resistant material is constructed from a platinum material.

1/1

Fig. 1

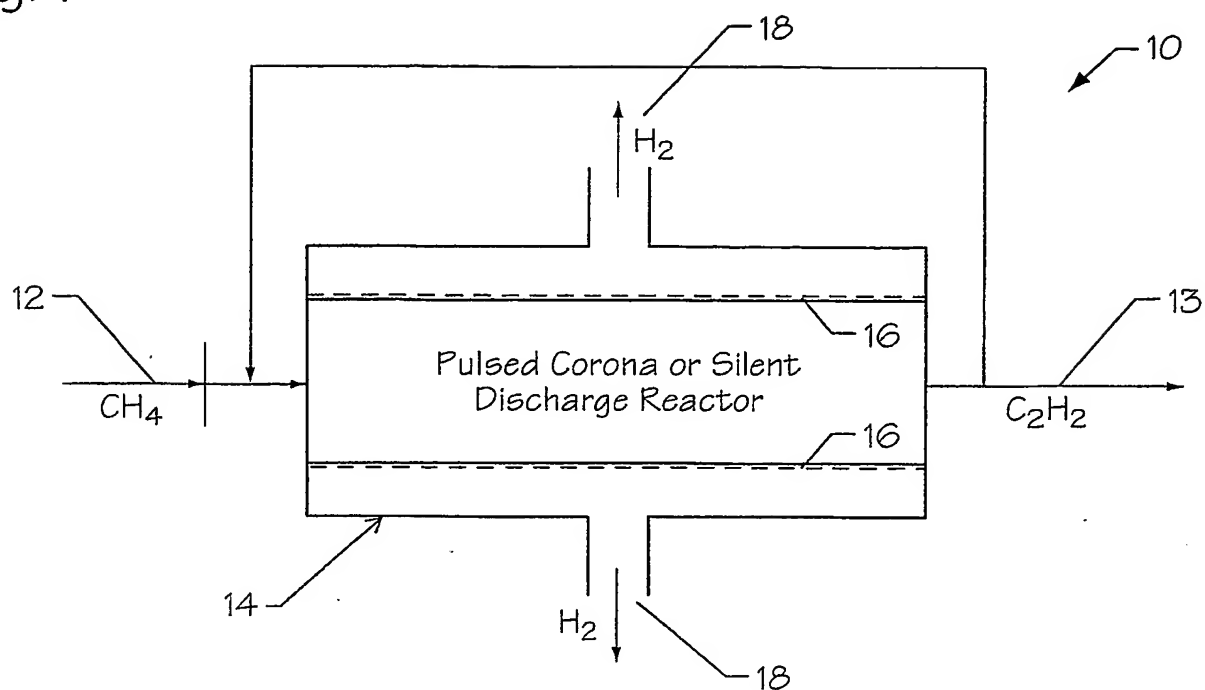
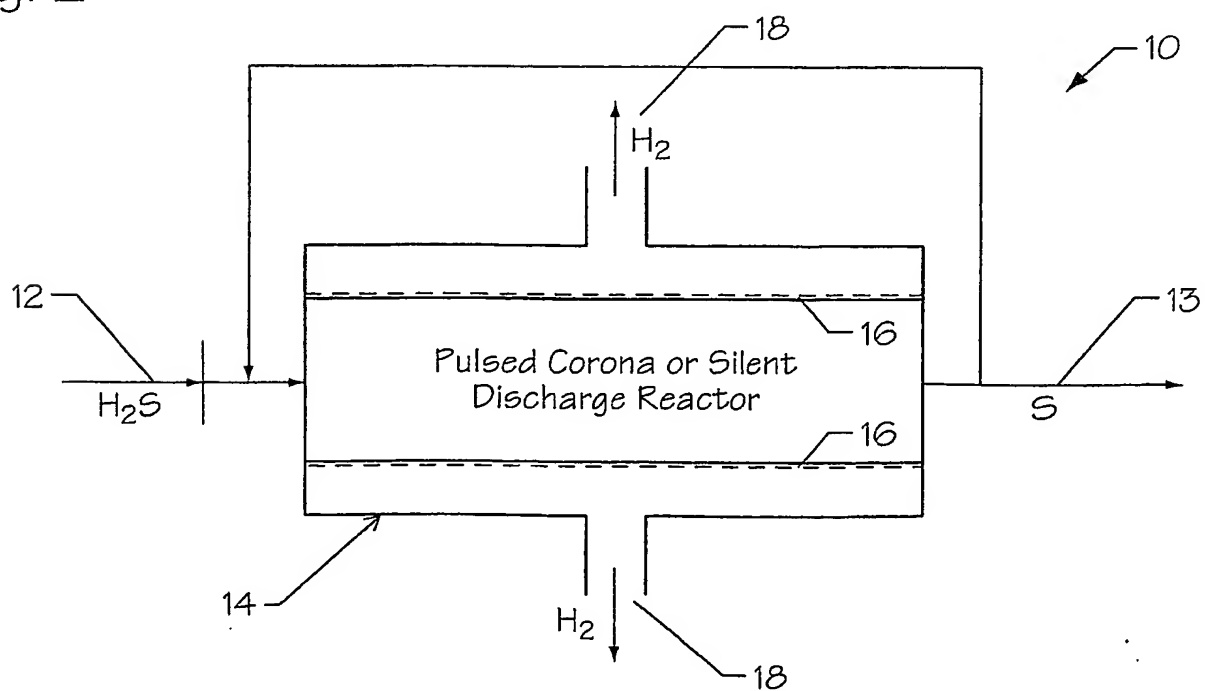


Fig. 2



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/30110

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) :B01J 19/08

US CL :204/164; 422/186.04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/164; 422/186.04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,933,608 A (HAAS et al.) 20 January 1976, see abstract , Fig. 1, col. 1, line 59 through col. 2, line 21.	34-51
Y	WO 98/28,223 A (ETIEVANT et al.) 02 July 1998, see abstract and Figs. 1 and 2.	7-10, 17-20, 39-42, 48-51
Y, P	US 6,245,309 A (ETIEVANT et al.), 12 June 2001, see entire document	34-51
X	US 3,280,018 A (DENIS) 18 October 1966, see Example 1, col. 4, lines 15-21 and col. 5, lines 29-30.	1-2, 11-12
--		-----
Y		3-10, 13-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

19 DECEMBER 2001

Date of mailing of the international search report

15 FEB 2002

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

KISHOR MAYEKAR DEBORAH THOMAS  
PARALEGAL SPECIALIST

Telephone No. (703) 308-0661

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/30110**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  
3+51

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/30110

### BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-20, drawn to method and apparatus for producing acetylene.

Group II, claim(s) 21-33, drawn to method for producing hydrogen.

Group III, claim(s) 34-51, drawn to method and apparatus for the production of hydrogen and elemental sulfur.

The inventions listed as Groups I-III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: All the groups are directed to apparatus and method (except group 2 to method only) useful in the general field of producing different chemical(s), but each group has a different special technical features. Group I has a special technical feature directed to a different reaction scheme not required for Groups II and III. Group II has a special technical feature directed to a different reaction scheme not required for Groups I and III. Group III has a special technical feature directed to a different reaction scheme not required for Groups I and II.